

# PATENT SPECIFICATION

(11) 1 586 067

1 586 067

(21) Application No. 44865/76 (22) Filed 28 Oct. 1976  
(23) Complete Specification Filed 27 Oct. 1977  
(44) Complete Specification Published 18 Mar. 1981  
(51) INT. CL.<sup>3</sup> C11D 1/66 //3/02 3/20  
(52) Index at Acceptance  
C5D 6A5D1 6A5D2 6A5E 6A5F 6A7 6B12C  
6B12M 6B12N1 6B13 6B1 6B2  
(72) Inventors: GUIDO BOGNOLI  
GERARD JEAN LICHTFUS  
CORNELIS JAKOB LUGTMEIJER

(19)



## (54) DETERGENT COMPOSITION

(71) We, THE PROCTER AND GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a detergent composition and, in particular, to a detergent composition suitable for use in automatic dishwashing machines and having good safety to surfaces characteristics.

Detergent compositions for use in automatic dishwashing machines generally contain 10 bleaching ingredients and relatively high levels of alkaline salts such as silicates, carbonates and phosphates. Typical examples of such compositions are to be found in U.S. Patent 3,598,743, issued August 10, 1971 to K. Coates and in U.S. Patent 3,888,781, issued June 10, 1975 to Kingry and Lahrman. Such compositions when used in a typical automatic dishwashing machine, have a tendency to harm certain surfaces, notably the surfaces of 15 coloured, glazed articles and of glassware. Thus, prolonged washing of such articles in an automatic dishwashing machine tends to result in a fading of colours on glazed articles and in slight etching of glassware. These deleterious effects are caused by a combination of the relatively high alkalinity which is typical of these products, the strong sequestering power of, for example the phosphate builder salts and the action of the bleaching agent.

20 It is known that certain materials can reduce the damage caused to these surfaces by detergent compositions of the automatic dishwashing machine type. For example, W. W. Niven, Jr. in "Industrial Detergents" (published by Reinhold New York (1955) at page 244 discloses the use of sodium aluminates, berylliates and zincates in dishwashing products to minimize the effect of the alkaline materials on surfaces. Also, D. Joubert and H. Van Daele, 25 Grasas Aceites (Seville), 1971, 22, 107 - 110 describes the effectiveness of soluble aluminate and alumino silicate salts in protecting the overglaze on china articles in an automatic dishwashing machine.

Unfortunately, it has been found that materials such as these, especially sodium aluminate, which are very effective at protecting overglaze on china articles have an undesirable effect 30 on glass surfaces in that they cause the glass to become somewhat iridescent and to take on a brownish hue. Also, it has been found that sodium aluminate can cause a slight reduction in the cleaning efficiency of such compositions. The basis of the present invention lies in the discovery that certain salts, which contain bismuth or antimony, when used in a detergent composition, provide good protection to china overglaze without demonstrating the negative 35 effect of causing iridescence on glassware, and without adversely affecting cleaning.

It is known from US patent 2,425,907 (Wyandotte Chemicals Corp.) that the addition of 40 various soluble chlorides, including bismuth and antimony chloride, to dilute aqueous solutions of sodium hydroxide, inhibits the tendency of the sodium hydroxide to attack glass surfaces. It has also been suggested, in Polish patent 44,942 (Kowalski et al) that antimony or bismuth salts could be incorporated into heavy duty detergents containing alkylaryl sulphophenates as the main detergent ingredient, and that these salts help to reduce the corrosion of laundry washing machines.

According to the present invention, there is provided a detergent composition for use in an 45 automatic dishwashing machine, comprising (a) a nonionic surfactant and (b) a salt containing bismuth or antimony, the solution pH as hereinafter defined of the composition being

5

10

15

20

25

30

35

40

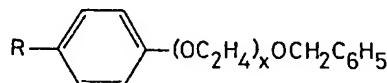
45

above pH 9.

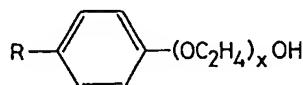
Preferably, the composition contains from 0.5% to 35%, more preferably 1% to 10%, of the nonionic surfactant and from 0.02% to 2%, more preferably from 0.05% to 1% of the bismuth or antimony-containing salt. The composition also normally contains alkaline builder salts such as phosphates and silicates, and preferably also contains a chlorine bleaching agent.

Detergent compositions according to the present invention contain a nonionic surfactant and, normally, this is the sole surfactant in the composition for the reason that compositions suitable for use in dishwashing machines must exhibit very low sudsing characteristics, and nonionic surfactants are the most suitable for this purpose. However, it is not excluded that certain quantities of other surfactants selected from anionic, zwitterionic, amphoteric, ampholytic and cationic surfactants are additionally present.

Nonionic surfactants which are advantageously employed in the composition of this invention include, but are not limited to, the following polyoxyalkylene nonionic detergents: C<sub>8</sub>-C<sub>22</sub> normal fatty alcohol-ethylene oxide condensates, i.e. condensation products of one mole of a fatty alcohol containing from 8 to 22 carbon atoms with from 2 to 20 miles of ethylene oxide, polyoxypropylene-polyoxyethylene condensates having the formula HO(C<sub>2</sub>H<sub>4</sub>O)<sub>y</sub>(C<sub>3</sub>H<sub>6</sub>O)(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>, H where y equals at least 15 and (C<sub>2</sub>H<sub>4</sub>O)<sub>z</sub>, equals 20-90% of the total weight of the compound; alkyl polyoxypropylene-polyoxyethylene condensates having the formula RO-(C<sub>3</sub>H<sub>6</sub>O)(C<sub>2</sub>H<sub>4</sub>O)<sub>y</sub>H where R is a C<sub>1</sub>-C<sub>15</sub> alkyl group and x and y each represent an integer from 2 to 98; polyoxyalkylene glycols having a plurality of alternating hydrophobic and hydrophilic polyoxyalkylene chains, the hydrophilic chains consisting of linked oxyethylene radicals and the hydrophobic chains consisting of linked oxypropylene radicals, said product having three hydrophobic chains, linked by two hydrophilic chains the central hydrophobic chain constituting 30% to 34% by weight of the product, the terminal hydrophobic chains together constituting 31% to 39% by weight of the product, the linking hydrophilic chains together constituting 31% to 35% by weight of the product, the intrinsic viscosity of the product being from 0.06 to 0.09 and the molecular weight being from about 3,000 to 5,000 (all as described in US patent 3,048,548); butylene oxide capped alcohol ethoxylates having the formula R(OC<sub>2</sub>H<sub>4</sub>)<sub>y</sub>(OC<sub>4</sub>H<sub>9</sub>)<sub>x</sub>OH where R is a C<sub>8</sub>-C<sub>18</sub> alkyl group and y is from 3.5 to 10 and x is from 0.5 to 1.5; benzyl ethers of polyoxyethylene condensates of alkyl phenols having the formula



where R is a C<sub>8</sub>-C<sub>20</sub> alkyl group and x is an integer from 5 to 40; and alkyl phenoxy polyoxyethylene ethanols having the formula



45 where R is a C<sub>8</sub>-C<sub>20</sub> alkyl group and x is an integer from 3 to 20. Other nonionic detergents are suitable for use in the herein disclosed dishwashing compositions and it is not intended to exclude any non-ionic detergent.

Preferred nonionic surfactants are the condensates of from 2 to 15 moles of ethylene oxide with one mole of a C<sub>8</sub>-C<sub>20</sub> aliphatic alcohol. Particularly preferred surfactants are those based on ethylene oxide condensates with primary aliphatic alcohols made by the "oxo" process. These alcohols are predominantly straight-chain aliphatic alcohols, with up to about 25% of short-chain branching at the 2-position. A suitable range of alcohol ethoxylates is made by the Shell Chemical Company and is sold under the trade name "Dobanol". A particularly preferred material of this type is Dobanol 45-4, which is the reaction product of 4 moles of ethylene oxide with 1 mole of a C<sub>14</sub>-C<sub>15</sub> oxo-alcohol. Another preferred commercially available range of surfactants is based on the ethoxylates of relatively highly branched alcohols, containing up to 60% of C<sub>1</sub>-C<sub>6</sub> branching at the 2-position. These alcohols are sold under the trade name "Lial" by Liquichimica Italiana. A preferred material is Lial 125-4, the condensation product of 4 miles of ethylene oxide with a C<sub>12</sub>-C<sub>15</sub> alcohol.

60 Detergent compositions of the present invention also comprise a salt which contains bismuth or antimony. Bismuth-containing salts are preferred for reasons of safety and availability. Particularly preferred materials are the trivalent bismuth or antimony halides, especially bismuth trichloride and bismuth citrate. Other bismuth salts which can be utilized in the present invention include bismuth sulphide, bismuth oxyhalide, bismuth subnitrate,

65

bismuth carbonate and bismuth acetate. Complex bismuth salts such as sodium bismuthate and sodium bismuth nitrite can also find application in compositions of the present invention. The corresponding antimony salts to the above-mentioned bismuth salts are also useful.

As indicated above, compositions of the present invention normally contain one or more alkaline salts and have a solution pH of above pH 9. The term "solution pH" as used in this specification means the pH in water of a 0.5 weight percent solution of the detergent composition.

The necessary solution pH of the composition may be achieved by the inclusion of any suitable substance, but preferably the composition comprises a substantial quantity of alkaline inorganic builder salts such as phosphates, carbonates and silicates. Particularly suitable inorganic builders include the alkali metal polyphosphates (for example sodium tripolyphosphate, pyrophosphate or hexametaphosphate), orthophosphates, carbonates, borates, and bicarbonates.

Water-soluble organic builder components may also be included. Examples of suitable organic alkaline detergency builder salts are: (1) water-soluble amino polyacetates, e.g., sodium and potassium ethylene-diaminetetra-acetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilotriacetates; (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates; (3) water-soluble polyphosphonates, including alkali metal salts of ethane-1-hydroxy-1,1-diphosphonic acid; methylenediphosphonic acid, ethylene diamine tetramethyl phosphonic acid and the like.

Additional organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent No. 2,264,103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent No. 3,308,067, incorporated herein by reference, are also suitable herein.

It is to be understood that while the alkali metal salts of the foregoing inorganic and organic polyvalent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium, alkanolammonium (e.g., triethanolammonium, diethanolammonium and mono-ethanolammonium) and other water-soluble salts of any of the foregoing builder anions can also be used.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts useful herein is the insoluble alumino silicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation  $Na_x(A1O_2)_{y}(SiO_2)_z \cdot xH_2O$  wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5 and x is an integer from 15 to 264. Compositions incorporating builder salts of this type form the subject of British Patent Specification No. 1,429,143 published March 24, 1976, German Offenlegungsschrift No. 2,433,485 published February 6, 1975, and Offenlegungsschrift No. 2,525,778 published January 2, 1976, the disclosures of which are incorporated herein by reference.

Highly preferred compositions of the present invention contain water-soluble silicates such as sodium, potassium and lithium silicates. Examples of suitable silicates are those which have an  $SiO_2$  to  $M_2O$  ratio of from 4:1 to 0.5:1, where M is an alkali metal. Such silicates can contain up to 50% by weight of water in the form of water of hydration. These include orthosilicates and metasilicates. Sodium metasilicate is a preferred material.

The total amount of alkaline salt in the composition can vary widely up to as much as 95% by weight. In preferred compositions, there is from 10% to 70%, especially 30% to 60% of phosphate or polyphosphate salts and from 20% to 60%, especially 30% to 45% of silicate salts, particularly sodium metasilicate.

While the preferred compositions contain these relatively large amounts of alkaline builder salts and are normally solid in form, it is also possible to prepare effective detergent compositions for automatic dishwashing machines which are in liquid or gel form and which contain little or no inorganic salt. In such cases, the necessary alkalinity can be achieved by the incorporation of, for example, amines such as monoethanolamine or triethanolamine.

Detergent compositions of the present invention also preferably include a bleach component. This component is included in the composition at a level sufficient to give the composition an available chlorine content of from 0.2% to 10%, preferably 0.5% to 5%. As used herein, the term "available chlorine" indicates the amount of chlorine in the composition which is equivalent to elemental chlorine in terms of oxidizing power. "Active chlorine" is often used instead of "available chlorine". The same type of chlorine is designated by the two terms, but when expressed quantitatively "active chlorine" indicates the chlorine actually present. The numerical value for available chlorine content is twice that for active chlorine.

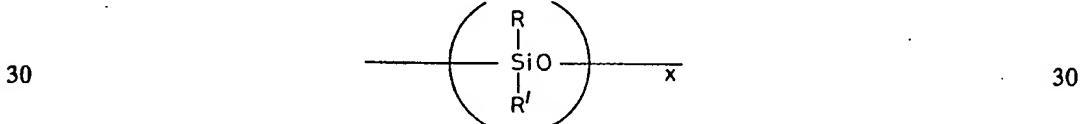
Available chlorine contents below 0.2% fail to give proper cleaning performance, while amounts in excess of 10% do not result in any added cleaning ability. Any of many known chlorine bleaches can be used in the present detergent composition. Examples of such bleach compounds are: chlorinated trisodium phosphate, dichloroisocyanuric acid, salts of chlorine substituted isocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N,N'-dichlorobenzoylene urea, paratoluene sulphodichloroamide, trichloromelamine, N-chloroammeline, N-chlorosuccinimide, N,N'-dichloroazodicarbonamide, N-chloroacetyl urea, N,N'-dichlorobiuret, chlorinated dicyandiamide, sodium hypochlorite, calcium hypochlorite, and lithium hypochlorite. The preferred bleach is an alkali-metal salt of dichloroisocyanuric acid, e.g. potassium or sodium dichloroisocyanurate.

Compositions of the invention can also advantageously include a glaze protecting agent in addition to the bismuth- or antimony-containing salt. While the essential bismuth or antimony salt does provide satisfactory protection against overglaze attack on its own, an enhancement of this protection can be achieved by including, for example, sodium aluminate in an amount from 0.05% to 2%. The ratio of bismuth chloride to sodium aluminate can be from 3:1 to 1:3. Preferably, this ratio is from 1:1 to 1:3, for example 1:2. It has been found that the deleterious effect of this material on glass is avoided or at least minimized in the presence of the bismuth or antimony salt.

Certain of the preferred surfactants of the present invention tend to over-suds in use and therefore preferred compositions include a suds suppressing agent.

Suds suppressing agents are normally used in an amount from 0.001% to about 6%, preferably 0.05% to 3%. The suds suppressing (regulating) agents known to be suitable as suds suppressing agents in detergent context can be used in the compositions herein.

Preferred suds suppressing agents are silicone materials which can be described as a siloxane having the formula



35 wherein x is from about 20 to 2,000, and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from 200 to 200,000, and higher, are all useful as suds controlling agents. The silicone suds suppressing agent is advantageously added in emulsified form and suitable emulsions are commercially available from Dow Corning 40 Corporation, sold under the trade names DB-31 and DEC-544.

40 Other useful suds suppressing agents include alkyl phosphate esters such as monostearyl phosphate and microcrystalline waxes having a melting point of from 65°C to 100°C and a molecular weight of from 400 to 1,000.

45 Neutral fillers such as sodium sulphate and sodium phosphate can be present and various other components can be included for various purposes. Examples of such additional components are enzymes, especially proteases and emylases (which are useful in the absence of chlorine bleach), tarnish inhibitors such as benzotriazole, bactericidal agents, soil-suspending agents, dyes and perfumes. Liquid, pasty or gel-like compositions normally contain solvents such as water and C<sub>1</sub>-C<sub>3</sub> alkanols.

50 Compositions of the invention can be prepared in any convenient way. For example, dry materials such as sodium tripolyphosphate and sodium silicate can be mixed together in a pan granulator while, with continuous mixing, the mixture is sprayed with an aqueous solution of sodium silicate to form a bed of agglomerated granules. The surfactant is sprayed subsequently onto the agglomerated granules. In a preferred method, the dry particulate components including all of the phosphate and silicate salts are mixed together in, for example, a drum or cube mixer or an inclined pan mixer. Then the liquid components, such as surfactant (as a melt if necessary), suds suppressor and perfume are sprayed onto the particulate mixture.

55 The compositions of the present invention are normally used in an automatic dishwashing machine at a concentration of from 0.1% to 1% in water.

60 Percentage values stated hereinbefore and hereinafter in this specification refer to a weight percentage of the total detergent composition.

65 The following examples are illustrative of the invention.

65 The following compositions were prepared by dry-mixing the solid ingredients in granular 65

form, and spraying the nonionic surfactant together with the suds suppressor onto the mixture.

	INGREDIENTS	EXAMPLES				5
		I %	II %	III %	IV %	
10	Sodium metasilicate	15.0	30.0	30.0	45.0	
	Trisodium orthophosphate		20.0			10
	Sodium tripolyphosphate	60.0	40.0	60.0	45.0	
	Dobanol 45-E-4	3.0	3.0	3.0	3.0	
15	Silicone suds suppressor	0.3	0.3	0.3	0.3	
	Sodium dichloroisocyanurate	2.0	2.0	2.0	2.0	15
	Sodium hexametaphosphate			2.5		
	Bismuth chloride			0.5	0.15	
20	Bismuth citrate	0.05	0.5			
	Sodium aluminate	0.05			0.35	20
	Sodium sulphate	12.0				
25	Moisture and miscellaneous		to 100			25

The above compositions were compared with similar compositions without bismuth salt and sodium aluminate and were found to offer significantly improved safety to decorated, glazed surfaces without any evidence of iridescence on glassware.

Further examples of compositions of the present invention are given below:

INGREDIENT	EXAMPLES										
	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
Sodium metasilicate	30	60	45	15	30	45	50	15	-	15	-
Sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O ratio 2.0)	-	-	15	-	10	-	10	-	20	-	20
Trisodium orthophosphate	20	-	-	20	15	-	10	15	30	-	30
Sodium tripolyphosphate	40	30	30	30	30	25	18	20	20	30	25
Sodium carbonate	-	-	-	10	-	10	-	5	-	5	-
C <sub>14</sub> -C <sub>15</sub> alkanol condensed with 7 moles of ethylene oxide	1.5	-	-	-	2.0	-	-	1.5	-	-	-
C <sub>12</sub> -C <sub>15</sub> alkanol condensed with 4 moles of ethylene oxide	-	3.0	2.0	-	-	4.5	7.5	-	-	-	-
Tallow alcohol condensed with 9 moles of ethylene oxide	-	-	-	2.5	4.0	-	-	-	-	1.5	3.0
Ethylene oxide/propylene oxide condensate of trimethylolpropane (Pluradot HA-433)	-	-	-	-	-	-	-	-	-	-	-
Silicone suds suppressor	-	0.3	-	-	0.4	0.5	0.5	1.0	-	0.15	0.3
Monostearic acid phosphate	-	-	-	0.2	-	-	-	-	-	-	-
Sodium hexametaphosphate	-	-	-	-	2.5	-	-	2.0	-	-	-
Sodium ethylene diaminetetraacetate	-	-	-	2.0	-	-	2.5	-	-	-	-
Sodium dichloroisocyanurate	2.0	2.0	2.0	1.0	2.0	3.0	-	-	-	-	-
Chlorinated trisodium orthophosphate	-	-	-	-	-	-	-	-	20	25	30
Sodium sulfate	-	-	-	1.5	-	-	-	30	-	20	-
Bismuth citrate	0.15	0.15	0.05	1.0	-	2.0	-	-	0.5	0.2	0.4
Bismuth trichloride	-	-	-	-	1.0	-	-	-	-	-	-
Sodium bismuthate	-	-	-	-	-	-	1.5	-	-	-	-
Antimony trichloride	-	-	-	-	-	-	0.6	-	-	-	-
Sodium aluminate	-	0.35	0.25	-	-	-	-	-	-	0.4	0.2
Moisture & Miscellaneous	-	-	-	-	-	-	-	to 100	-	-	-

All of the above compositions provide effective cleaning of dishes and utensils in an automatic dishwashing machine, without damaging decorated, glazed articles even after prolonged use and without causing iridescence on glassware.

WHAT WE CLAIM IS:-

5. 1. A detergent composition for use in automatic dishwashing machines comprising (a) a nonionic surfactant and (b) a salt containing bismuth or antimony, the solution pH as hereinbefore defined of the detergent composition being above pH 9. 5

2. A composition according to claim 1, wherein the said salt is bismuth citrate. 10

3. A composition according to claim 1, wherein the said salt is a halide of bismuth or antimony. 10

4. A composition according to claim 3, wherein the said salt is bismuth trichloride. 10

5. A composition according to any one of claims 1-4 wherein the nonionic surfactant is present in an amount of from 0.5% to 35%. 15

6. A composition according to claim 5, wherein the nonionic surfactant is a condensate of from 2 to 15 moles of ethylene oxide with a C<sub>8</sub>-C<sub>20</sub> aliphatic alcohol. 15

7. A composition according to any one of claims 1-6, wherein the said salt is present in an amount of from 0.02 to 2%. 15

8. A composition according to any of claims 1-7 comprising:  
 (a) from 1% to 10% of the nonionic surfactant, 20  
 (b) from 0.02% to 2% of the said salt and 20  
 (c) from 30% to 95% of an alkaline builder salt. 20

9. A composition according to claim 8, wherein the alkaline builder salt is selected from alkali metal phosphates, alkali metal polyphosphates, alkali metal silicates, and mixtures thereof. 25

10. A composition according to claim 9, wherein the alkaline builder salt comprises a mixture of from 30% to 60% of alkali metal tripolyphosphate and from 20% to 60% of alkali metal silicates. 25

11. A composition according to any one of claims 8-10, wherein the said salt is present in an amount of from 0.05% to 1%. 30

12. A composition according to any one of claims 1-11, which additionally comprises from 0.05% to 2% of sodium aluminate. 30

13. A composition according to any one of claims 1, 3 to 6 and 10 additionally comprising a chlorine bleach. 35

14. A composition according to any one of claims 2, 7 to 9, 11 and 12 additionally comprising a chlorine bleach. 35

15. A composition substantially as hereinbefore described with reference to any one of Examples III, IV and XI. 35

16. A composition substantially as hereinbefore described with reference to any one of Examples I, II, V to X and XII to XV. 40

17. A process for washing objects in an automatic dishwashing machine comprising contacting the objects in the machine with from 0.1% to 1% of an aqueous solution of the composition of any one of claims 1, 3, to 6, 10 and 15. 40

18. A process for washing objects in an automatic dishwashing machine comprising contacting the objects in the machine with from 0.1% to 1% of an aqueous solution of the composition of any one of claims 2, 7 to 9, 11, 12 and 16. 45

For the Applicants:-

CARPMAELS & RANSFORD,  
 43 Bloomsbury Square,  
 London WC1A 2RA.